More progress on PM characterization with X-ray techniques

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Carbon XANES

Last year: X-ray absorption (XANES) of **single** diesel soot **particles** with microscope (STXM), published in *FUEL*.

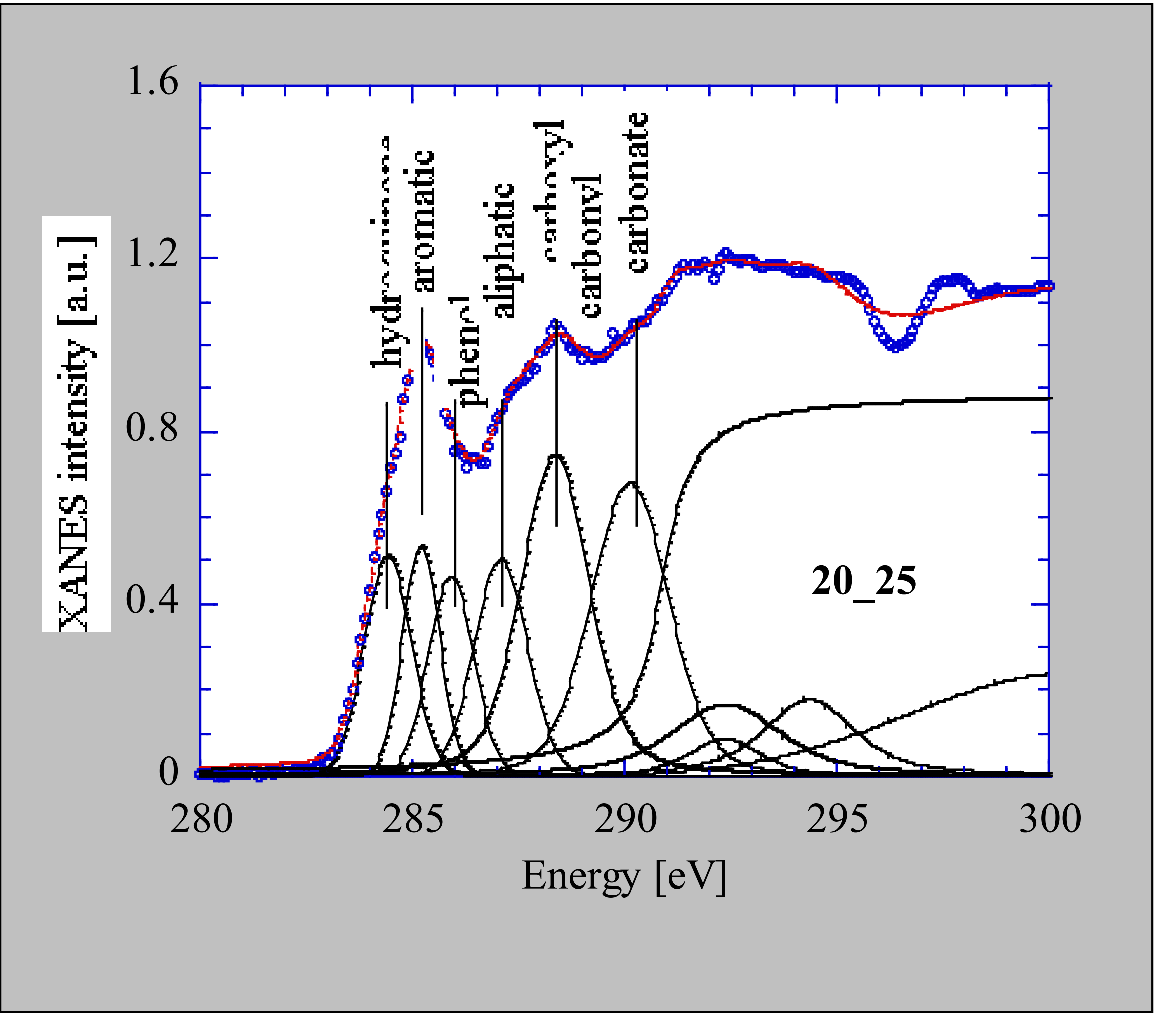
Then: Conventional, faster bulk XANES (not single particles, but powder, pellets), to confirm STXM results.

- Utah diesel soot
- Ford diesel soot
- LRRI wood smoke
- Ethylene soot
- ambient Whalen PM
- NIST 1650 standard diesel soot
- ambient ceiling fan dust
- Jet PM

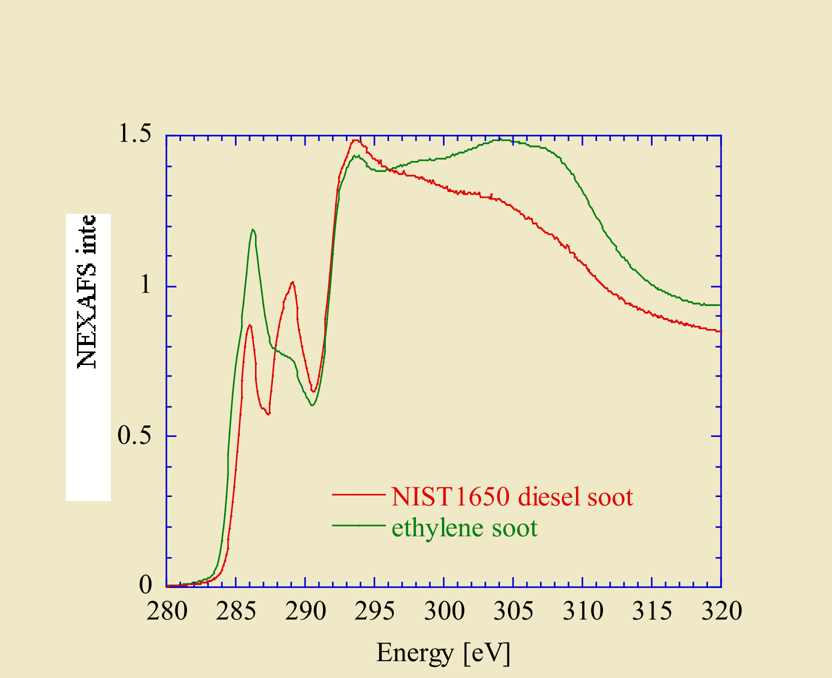
Then: STXM on the extracts (sub-critical water, 25^{o}C – 300^{o}C) of Utah diesel soot

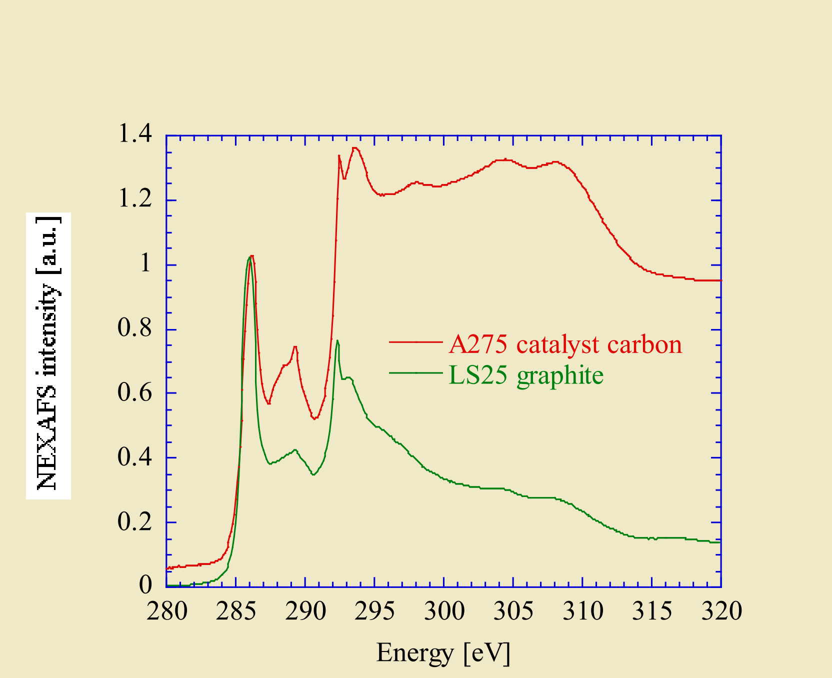
Assignment of carbon K-shell absorption peaks (attempted !)

Assignment of peaks not trivial. Significant number of reference spectra from organics and inorganics required for meaningful catalogue.
Has not been done yet.



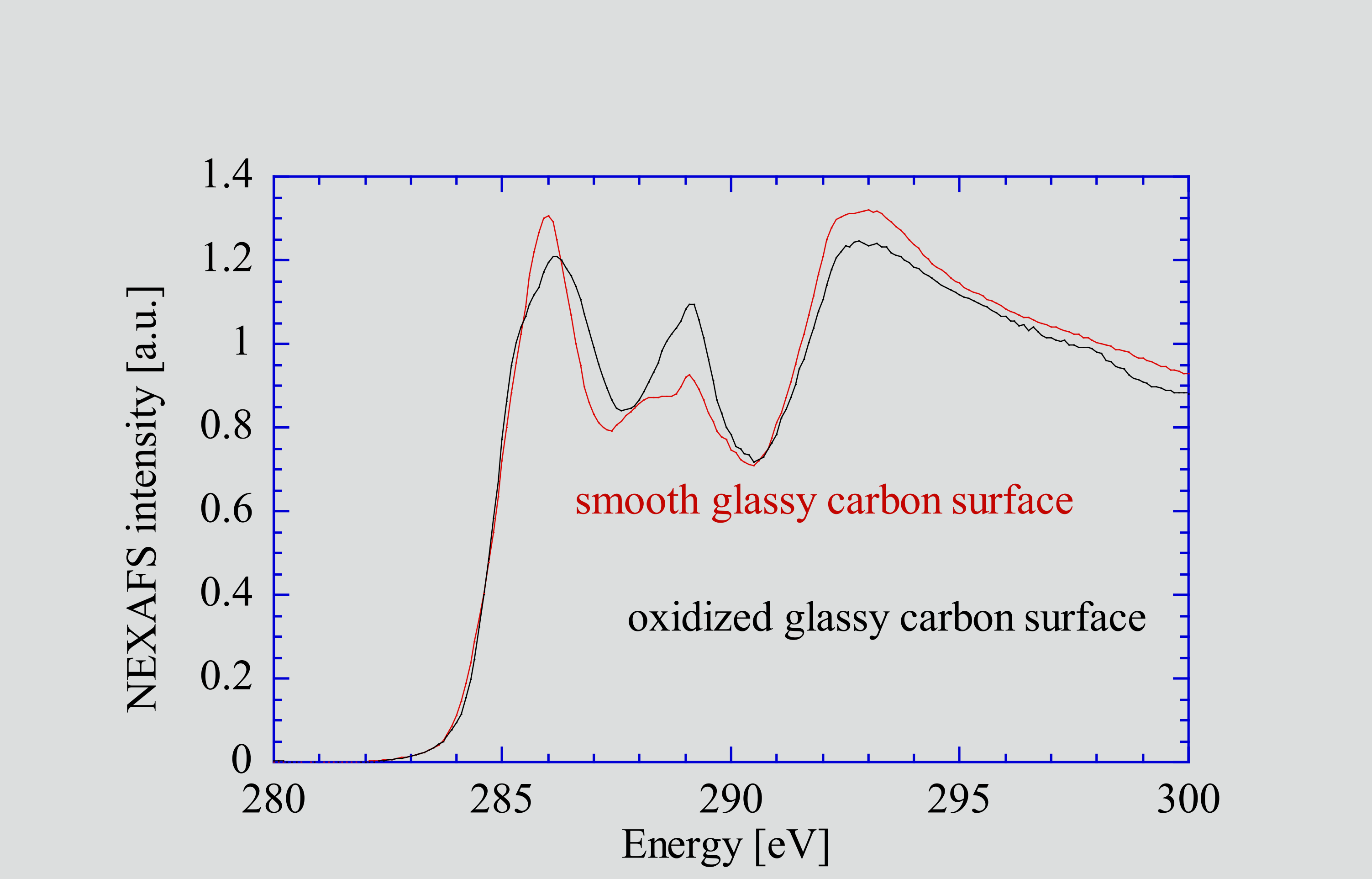
Ethylene /air flame soot vs. diesel soot, graphite..





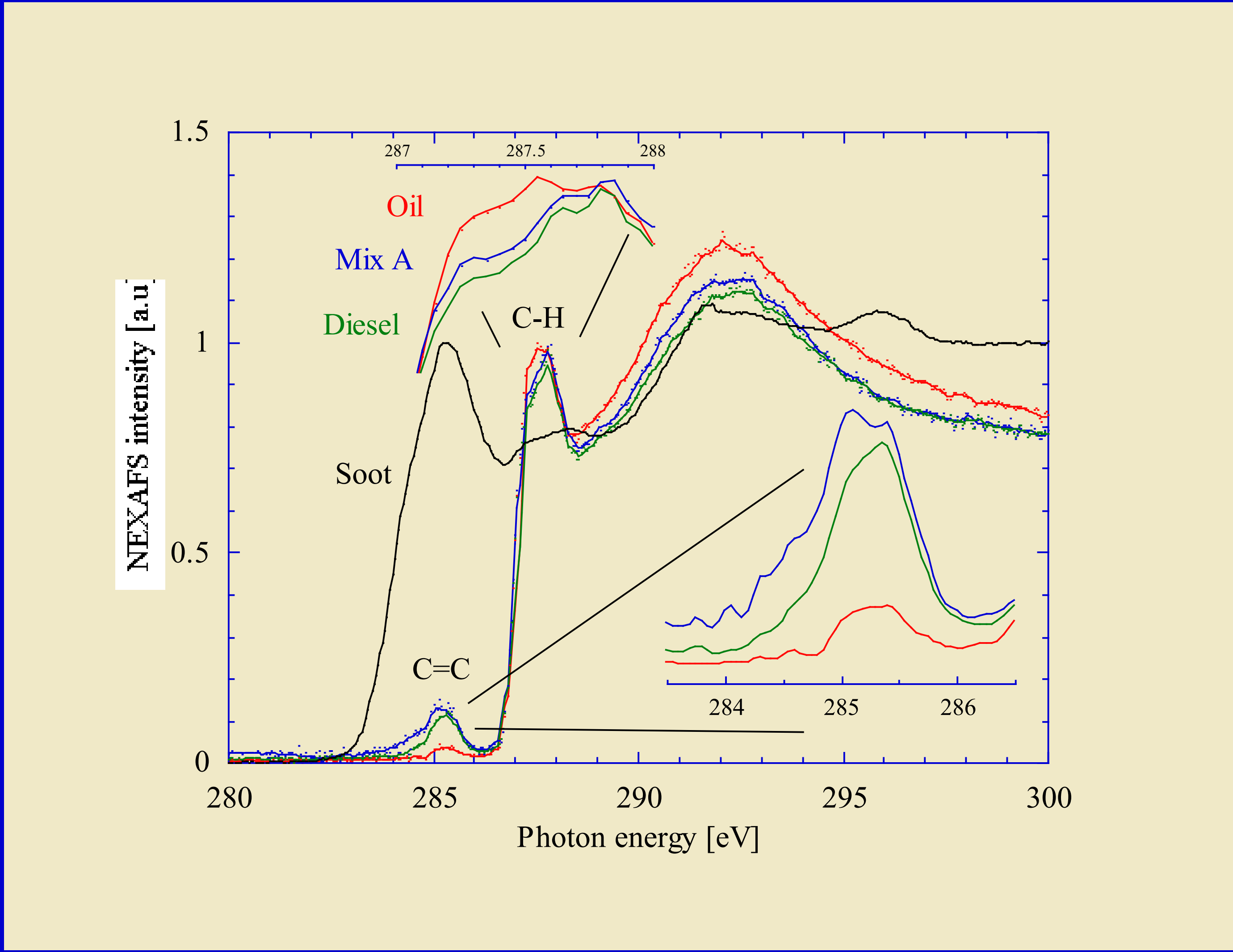
Soot, carbon black, and graphite have much in common in terms of their NEXAFS spectra.

Oxidation of glassy carbon

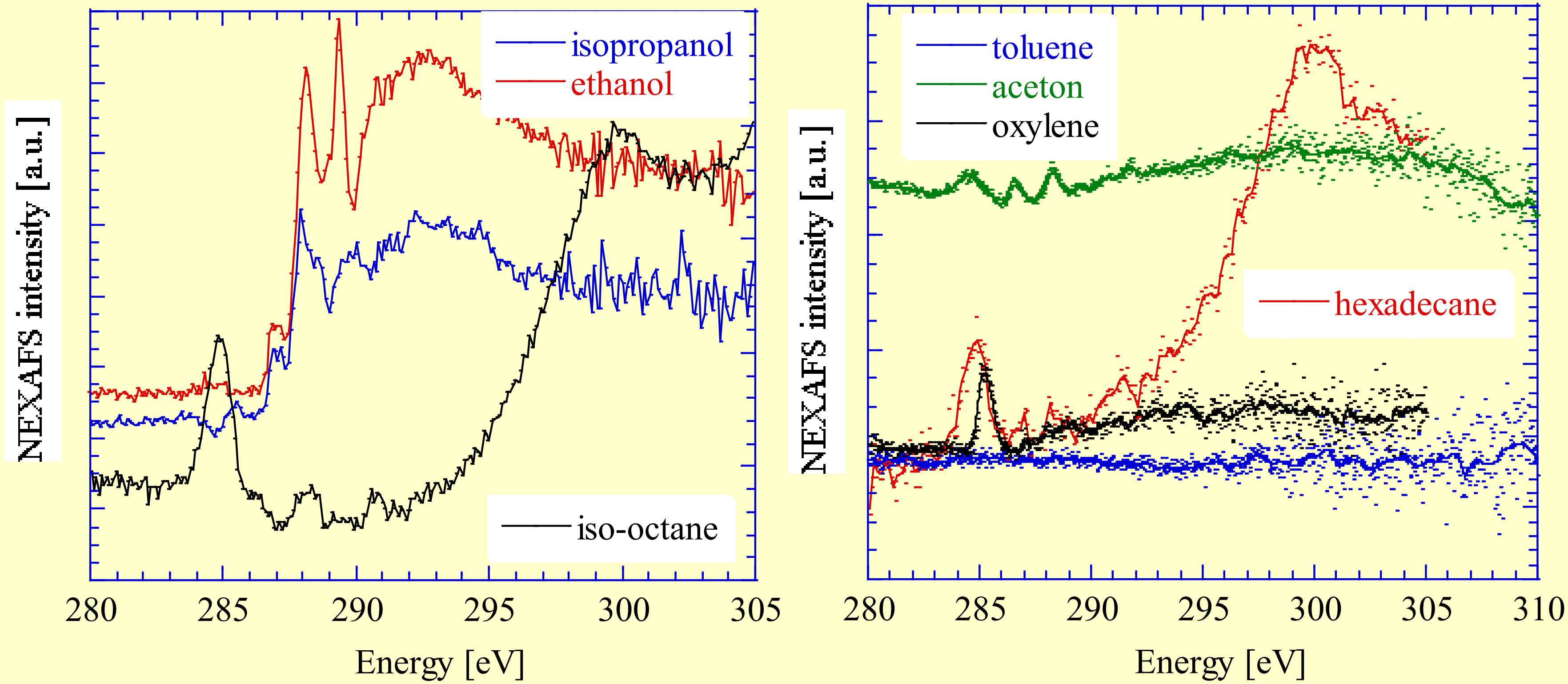


Oxidation removes aromatic C=C bond material; enhances phenol and carboxyl

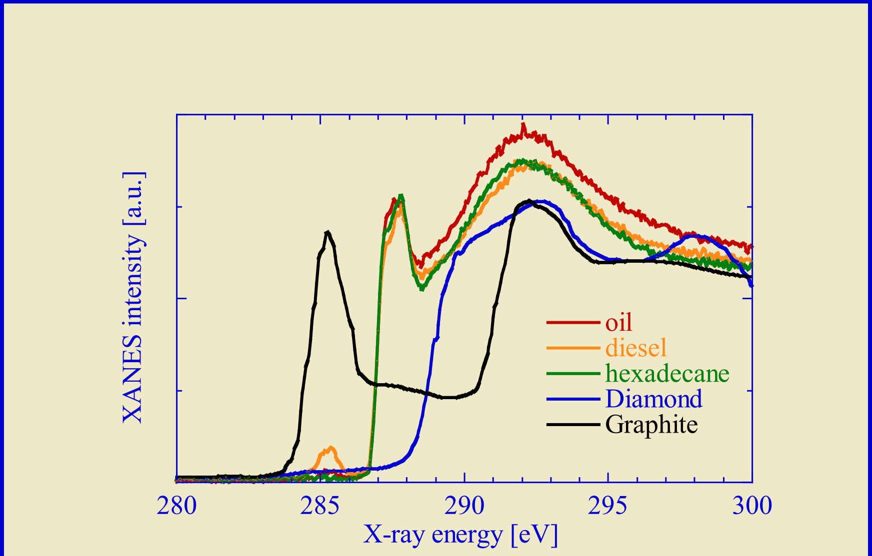
XANES of oil, diesel, soot

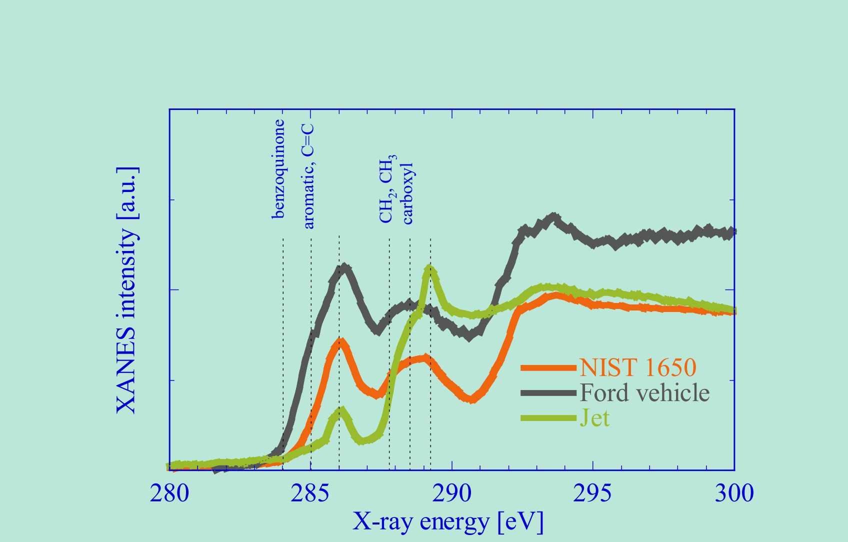


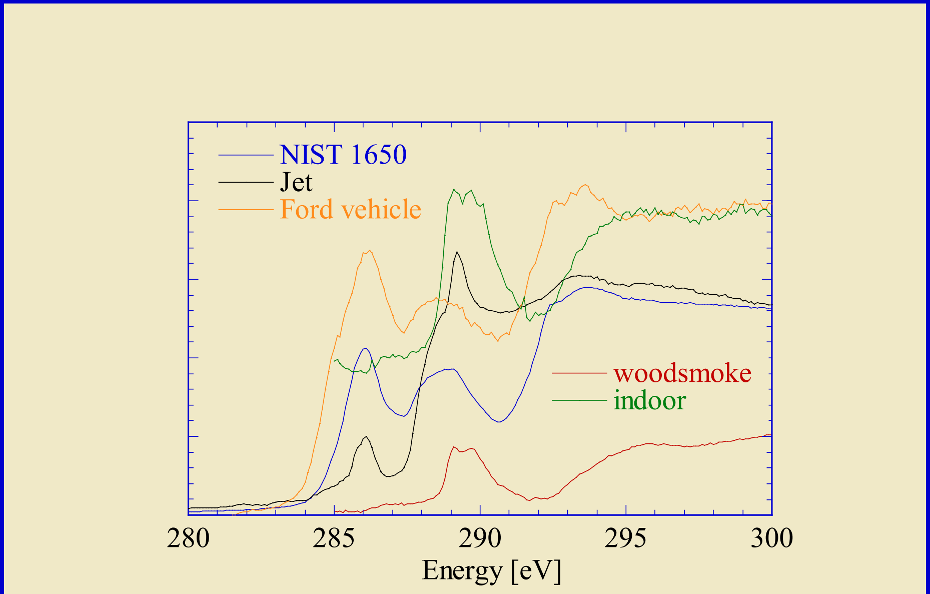
XANES of some organic reference materials



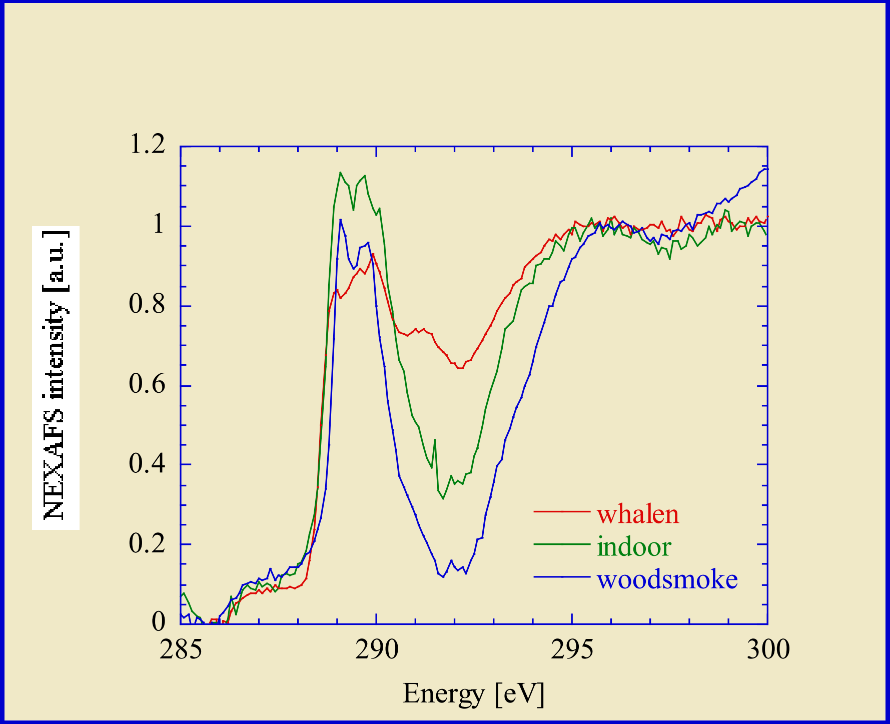
More XANES


XANES intensity [a.u.]
X-ray energy [eV]
280
285
290
295
300
oil
diesel
hexadecane
Diamond
Graphite


XANES intensity [a.u.]
X-ray energy [eV]
280
285
290
295
300
benzoquinone
aromatic, C=C
CH2, CH3
carboxyl
NIST 1650
Ford vehicle
Jet


Energy [eV]
280
285
290
295
300
NIST 1650
Jet
Ford vehicle
woodsmoke
indoor

Woodsmoke and ambient PM samples

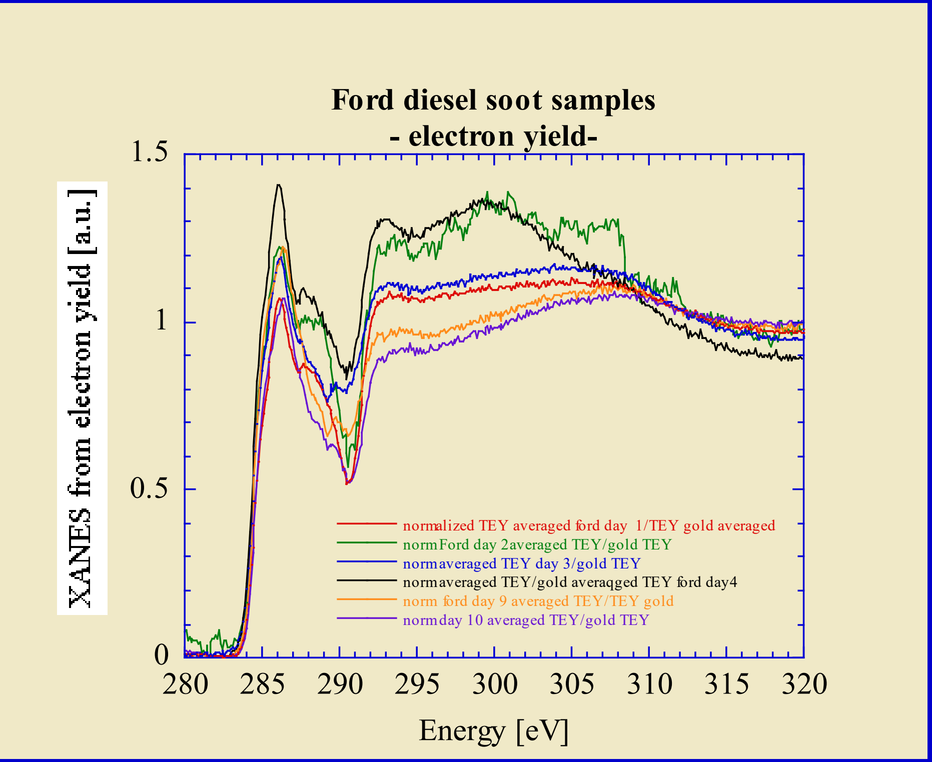


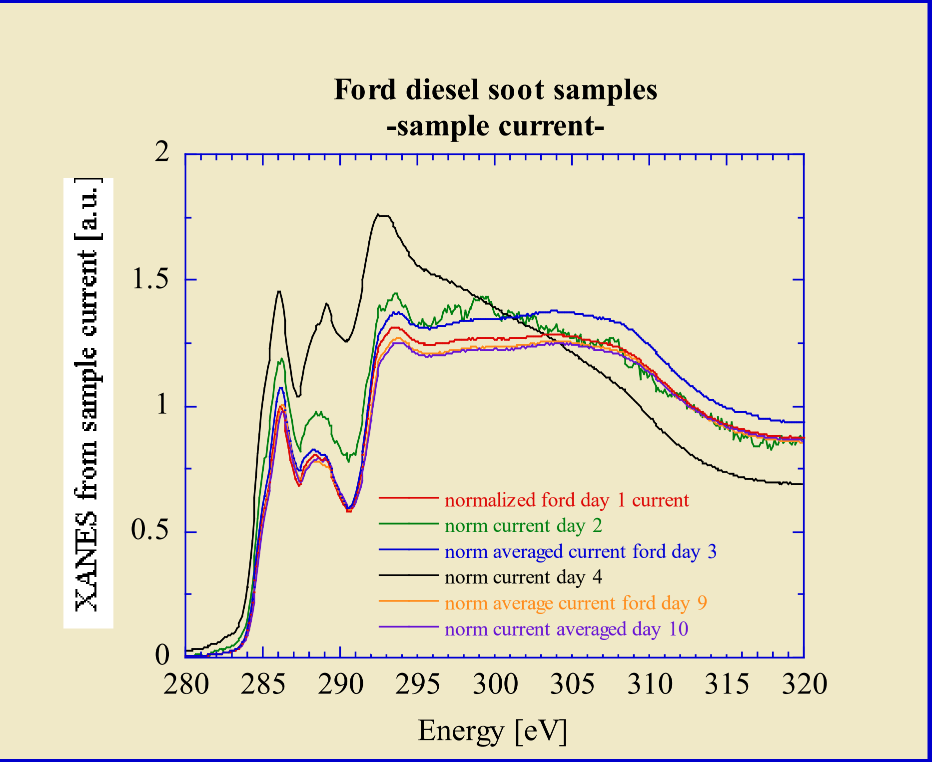
- Indoor/Dust from ceiling fan
- Whalen ambient PM
- LRRI wood smoke

Show a remarkable similarity; area here rich in limestone; maybe CaCO3 ? Ca absorption edges present in all these samples at 350 eV. Carbonate shows a peak 290 eV; Carbonyl at 289 eV.

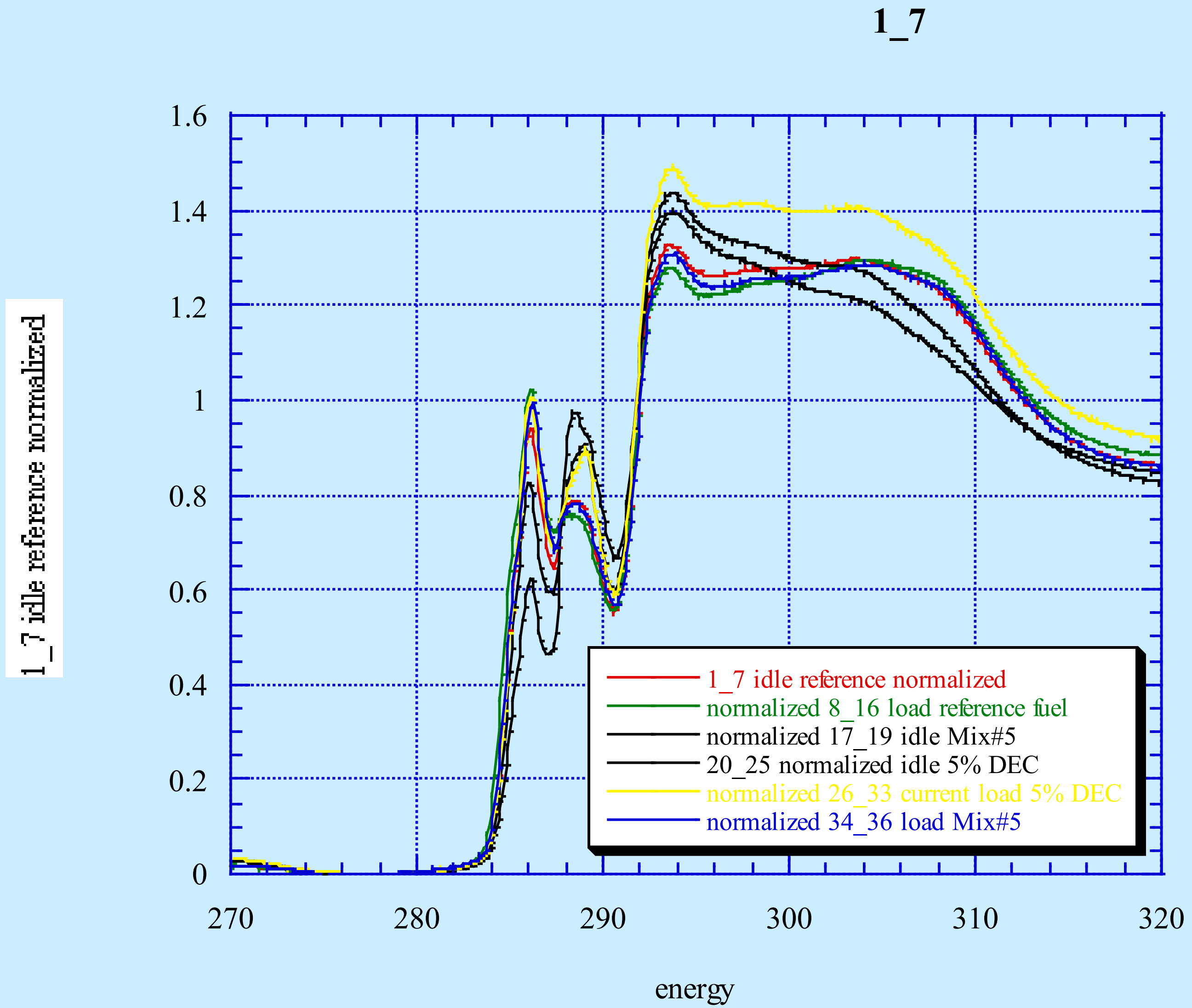
Soot from a Ford passenger vehicle electron yield vs. sample current detection mode

1998 diesel, 1.9 l/4 cyl, turbo, injection, cat, 1998 CA emission standards

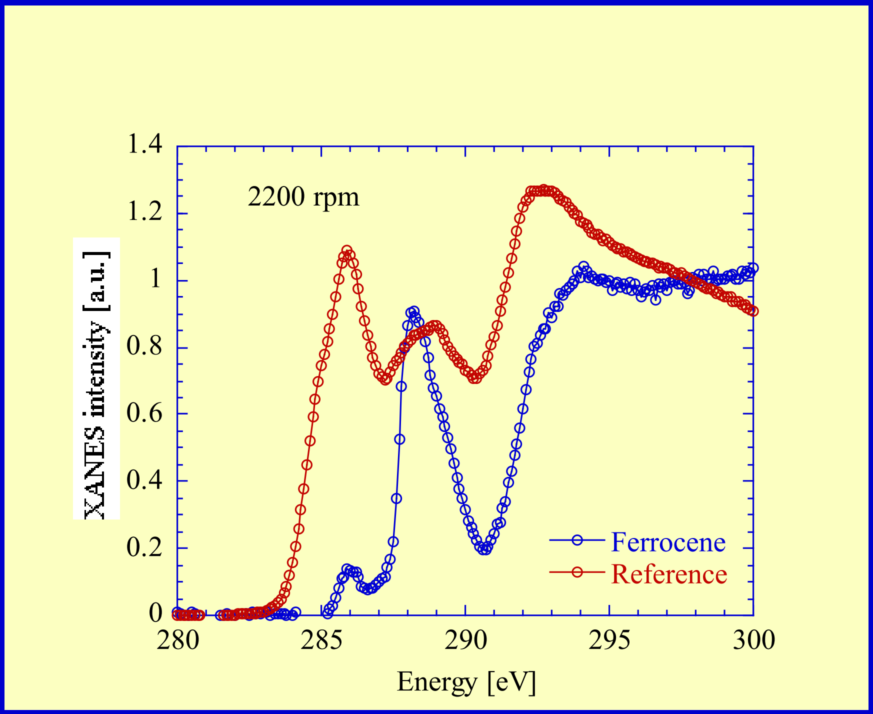


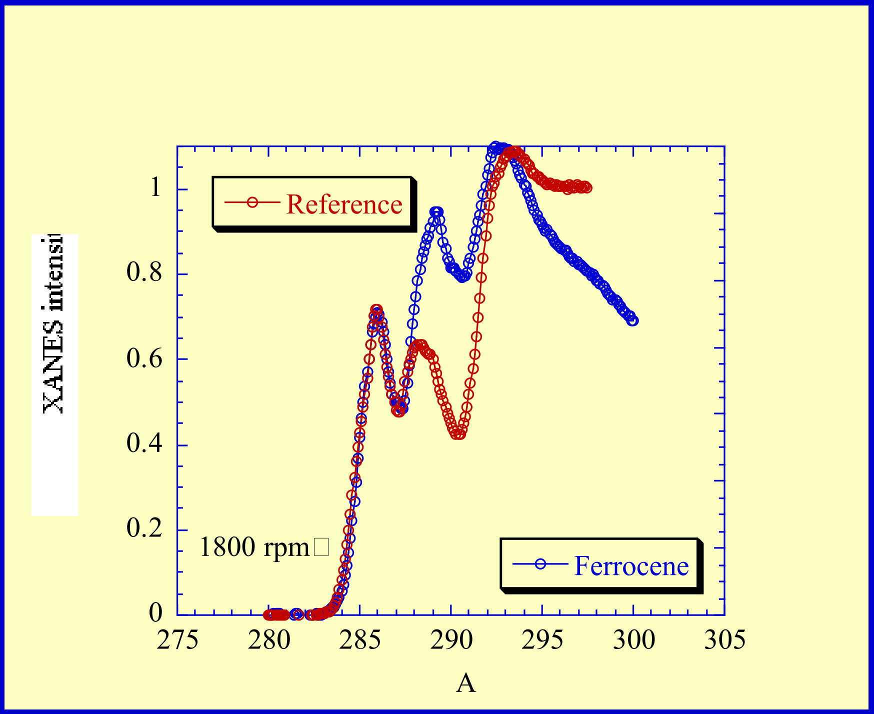


Comparison of "old" Utah diesel soot



Soot from ferrocene treated diesel fuel





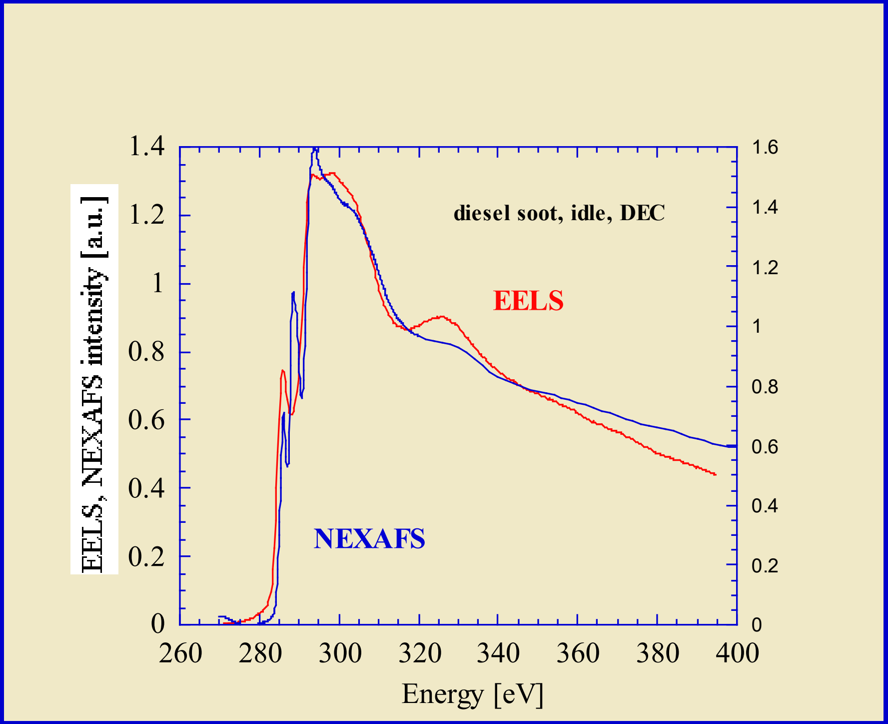
Ferrocene reduces C=C bonds, but aliphatic and carboxyl groups increase.

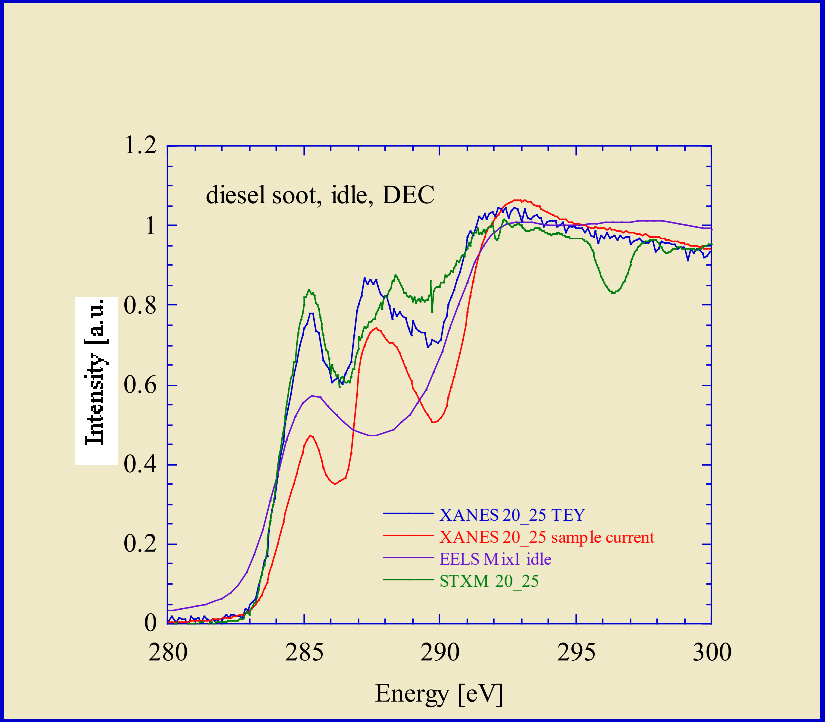
EELS vs. NEXAFS

Many electron microscopes come with an electron spectrometer, and the EELS spectra come thus "for free".

EELS = popular, many applications, many publications, incl. carbon.

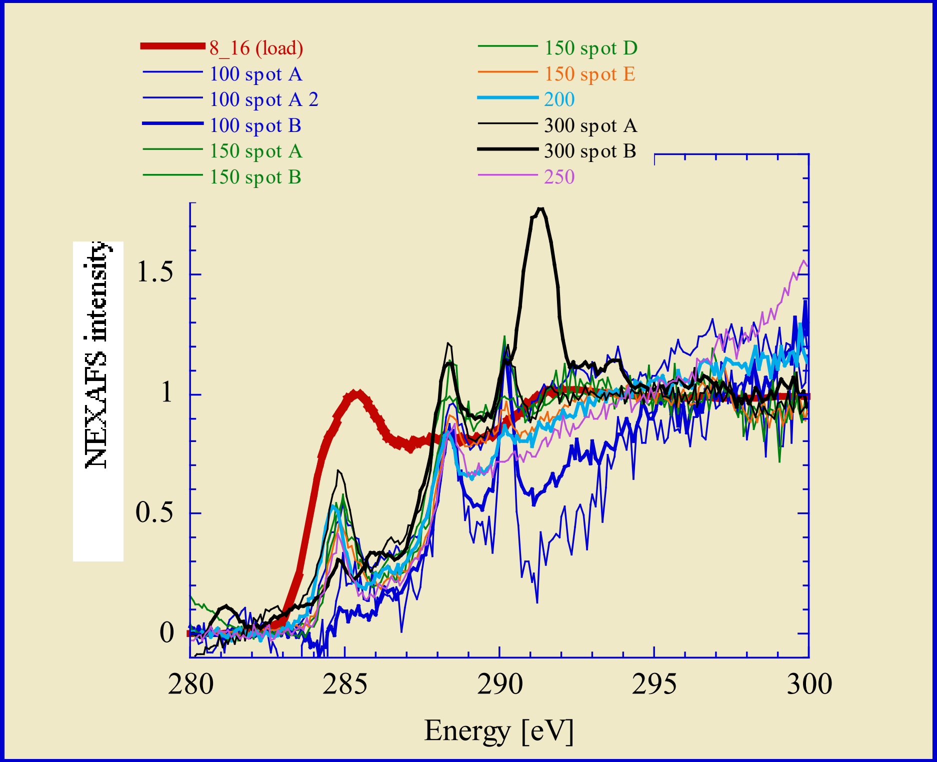
But: we find EELS is blind for some key features in the molecular structure, which are visible for XANES !

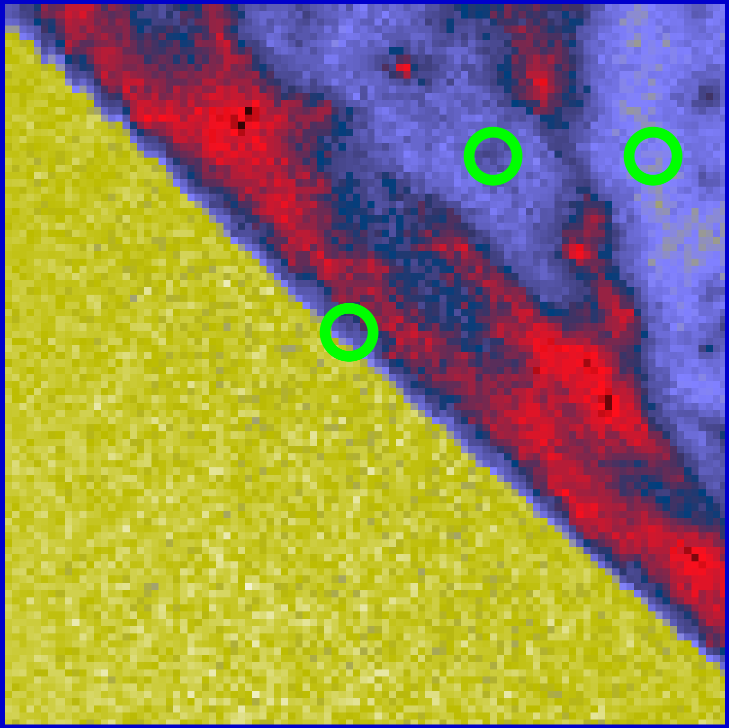




NEXAFS of diesel soot extracts

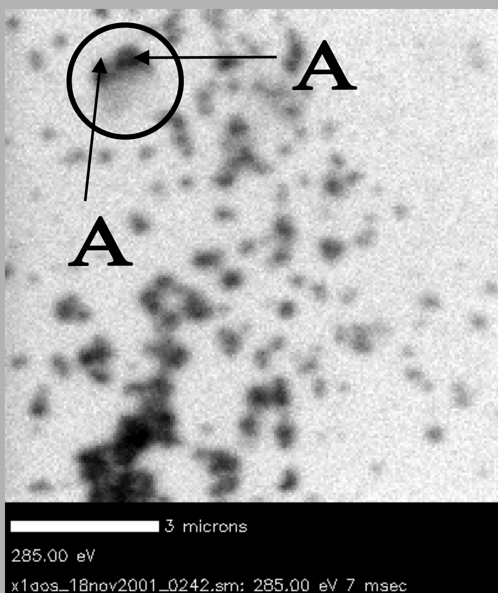
Extraction with sub-critical water; extracts measured with STXM; Particular points on dried extract selected and measured; some inhomogenity found. Analysis in progress.

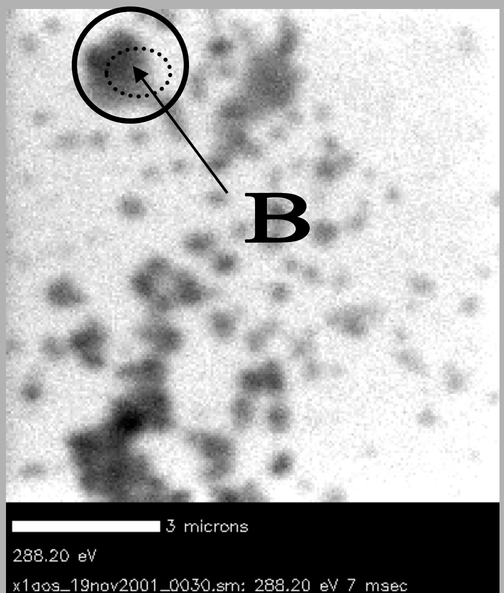


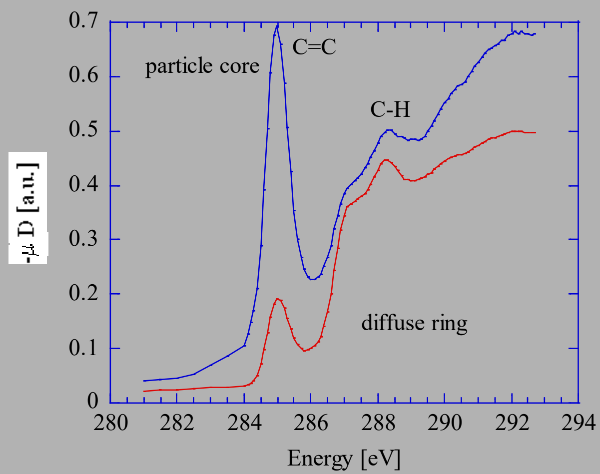


Recall from previous meeting
Scanning Transmission X-ray Micro-spectroscopy - “STXM”

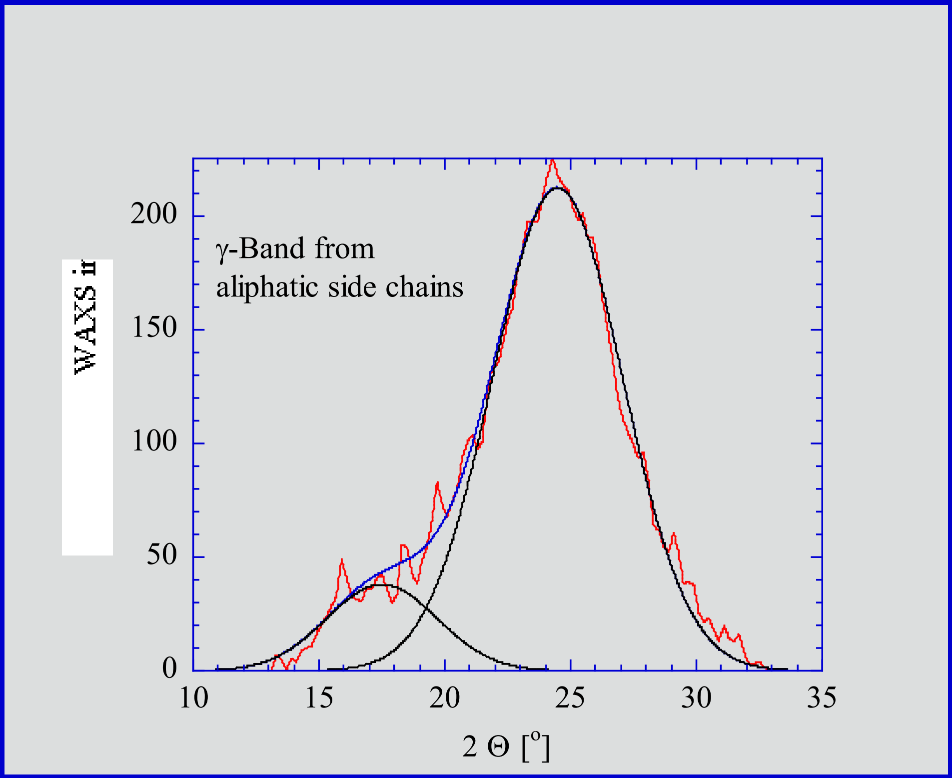
Contrast-variation between aromatic and aliphatic carbon due to different X-ray absorption







Wide-angle X-ray scattering of soot



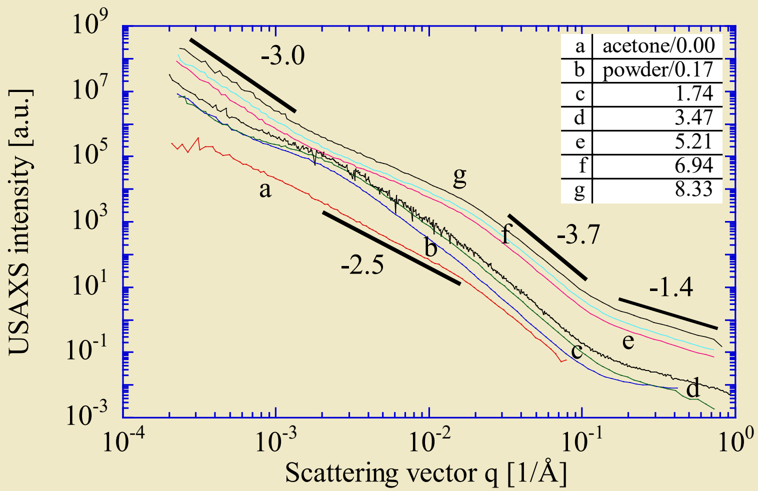
WAXS/XRD studies well known for coal
Aromaticity can be obtained from WAXS

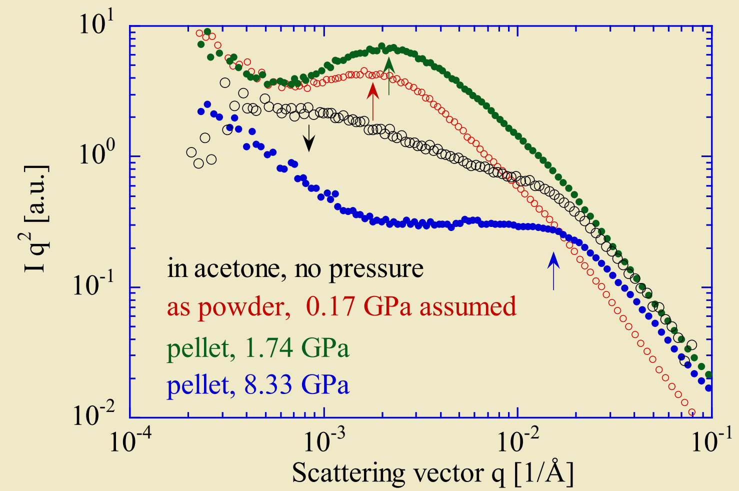
Problem: soot contains volatiles; difficult to distinguish solid soot core from volatiles

Extraction by sub-critical water, then WAXS

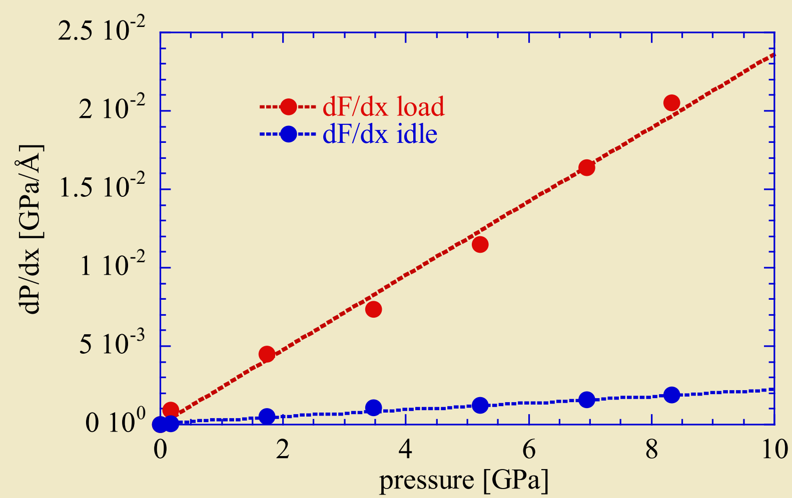
WAXS is almost everywhere available; good candidate for organic/black carbon determination

Elasticity of soot probed by USAXS



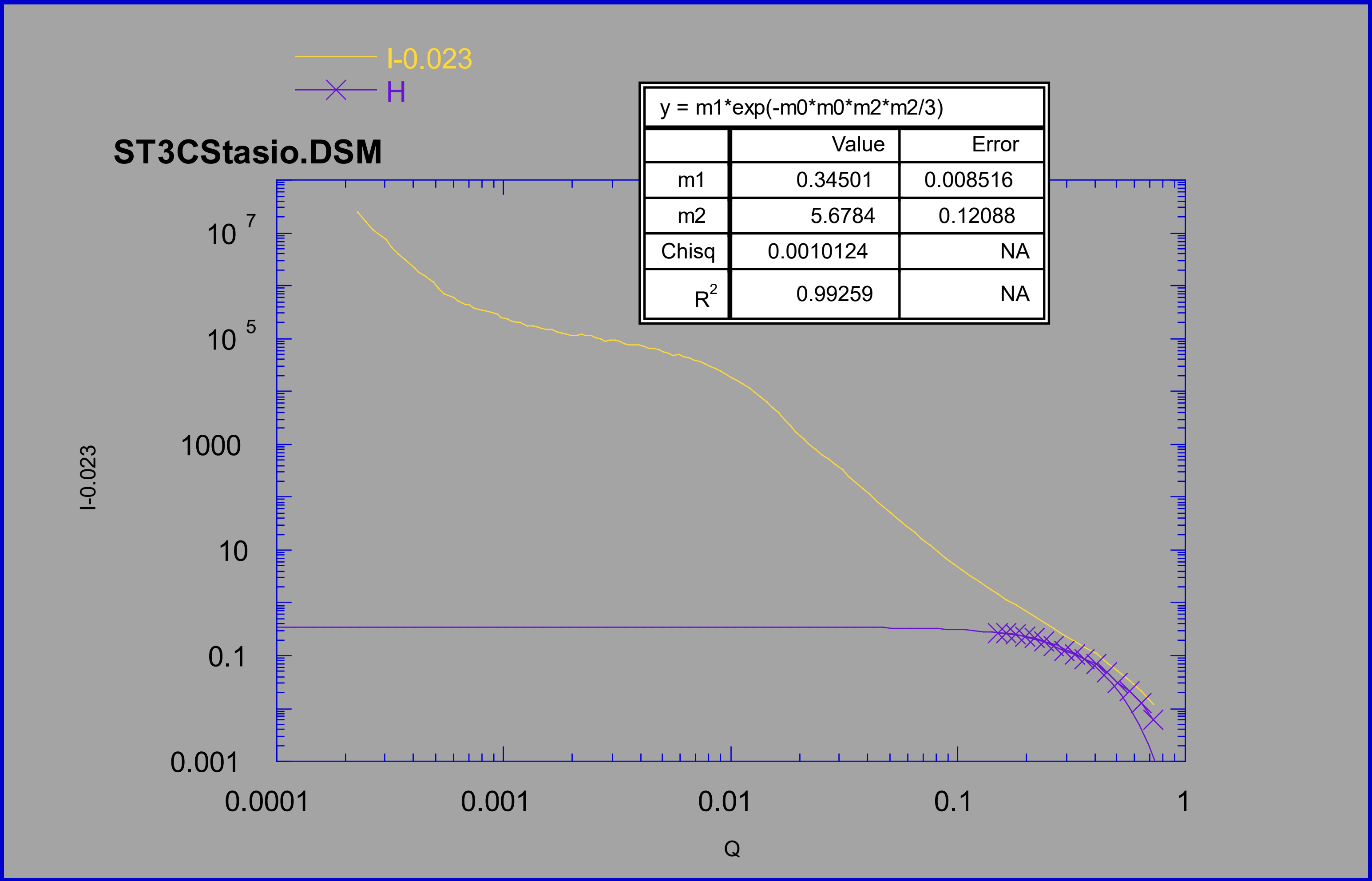


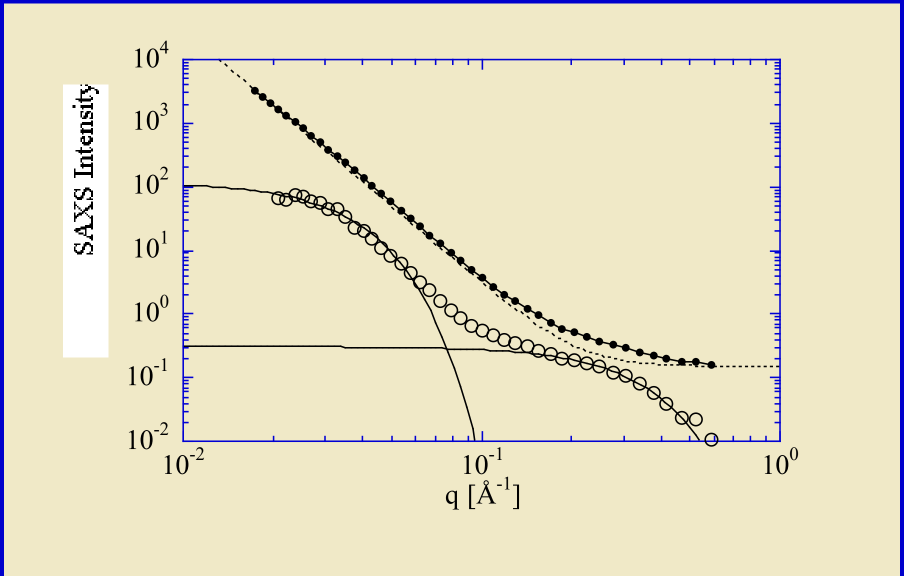
- Diesel soot from idle and load engine was studied as 1) powder, 2) pressed pellets, and 3) in acetone with USAXS.
- Soot aggregates become more compact when pressure increases, as evidenced by Kratky plot.
- This is a novel approach to remove scattering contamination from aggregate structures, and opens path to identify primary particles.
- Quantitative analysis permits to assign a Hooke's *constant*, which is a linear function of applied pressure.
- Size and elastic properties of soot may be useful thermodynamic parameters (heat-capacity) for energy inventory calculations and modeling.
- Scattering curves from soot can be well modeled/fitted with form factors of star polymers, revealing structural similarity of soot and star-polymers.

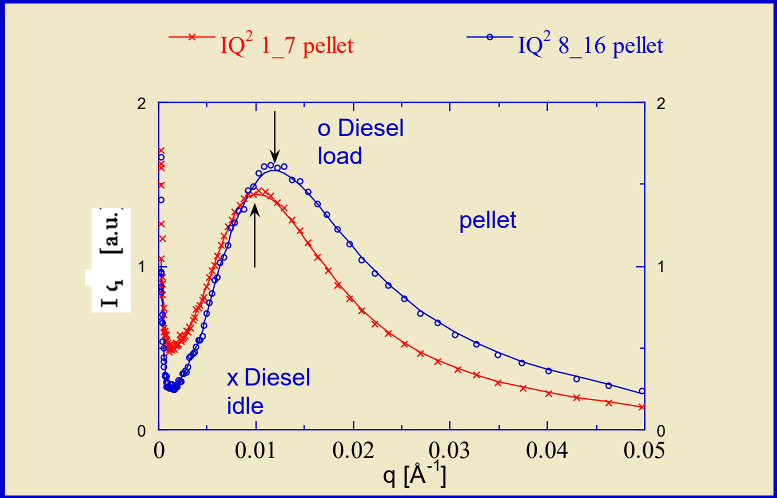


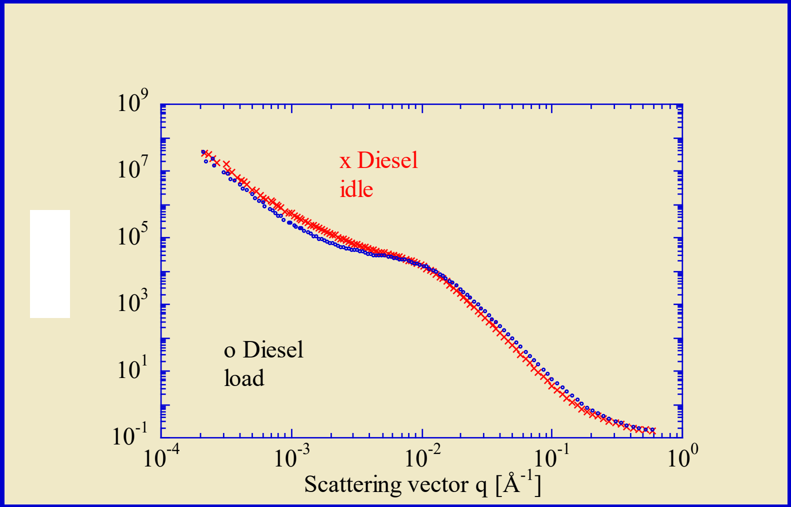
Consortium for Fo

Propane/air soot USAXS

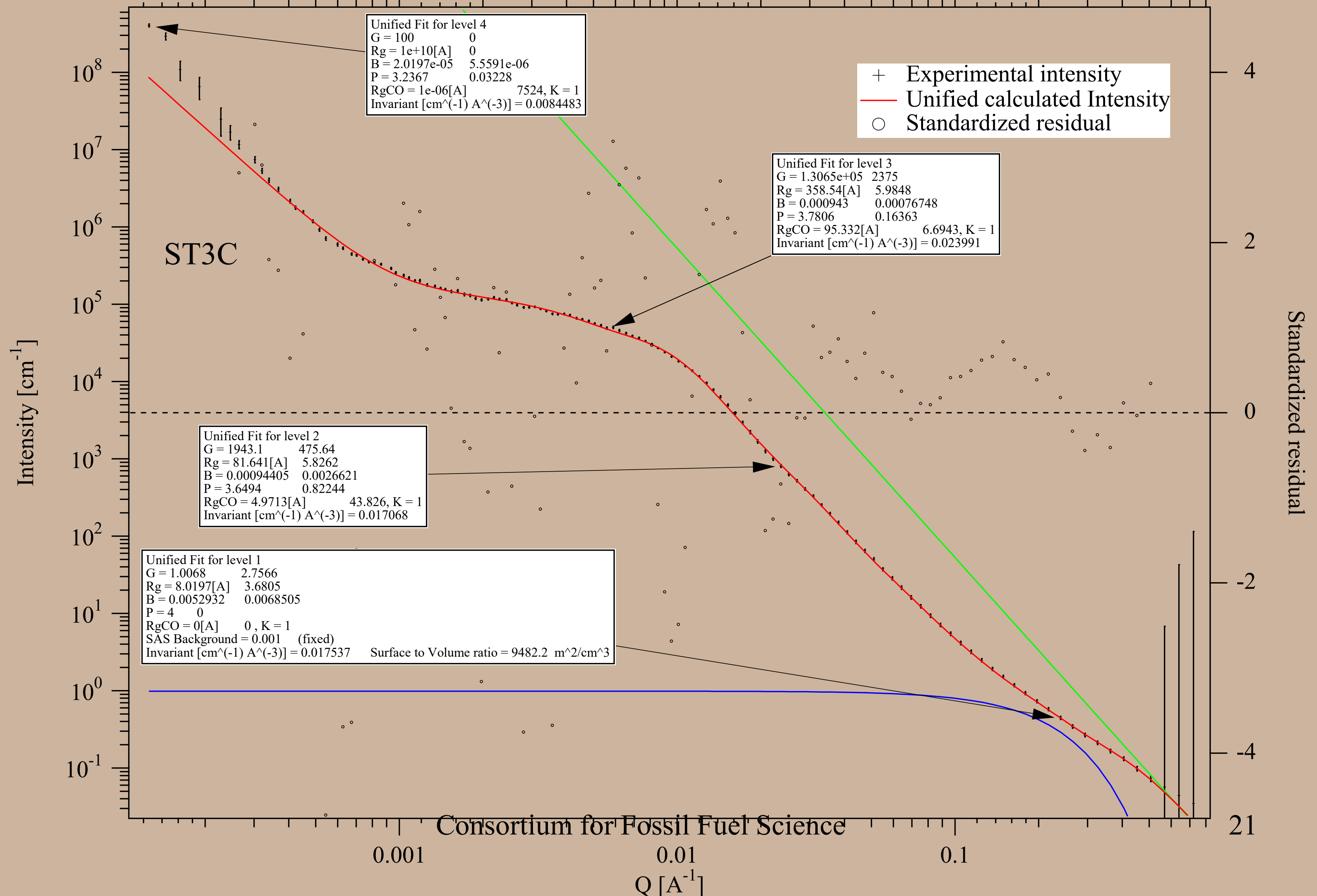



SAXS Intensity
10^4
10^3
10^2
10^1
10^0
10^{-1}
10^{-2}
10^{-2}
10^{-1}
10^0
q [Å^{-1}]

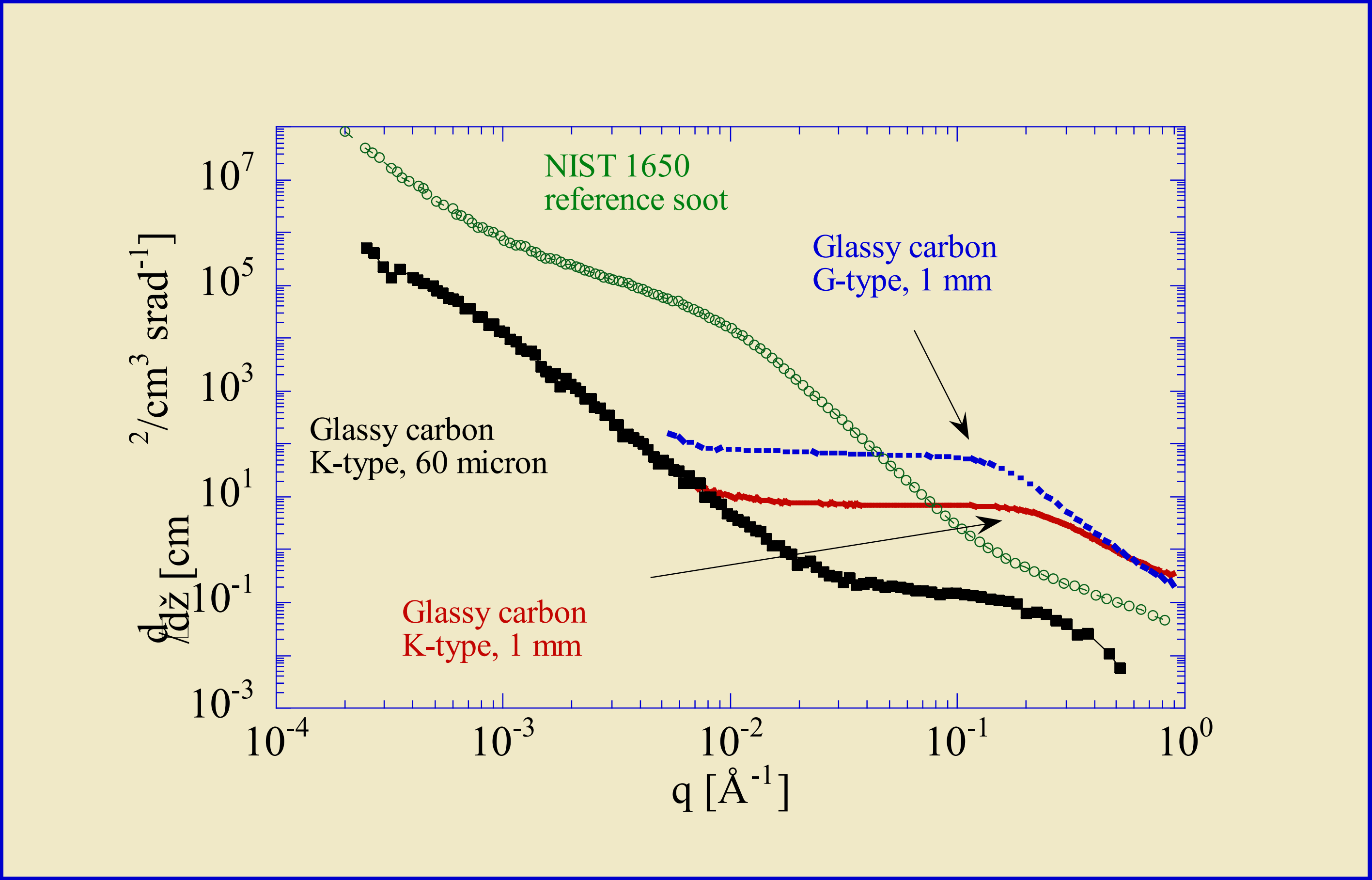

IQ^2 1_7 pellet
IQ^2 8_16 pellet
o Diesel load
pellet
x Diesel idle
[a.u.]
q [Å^{-1}]
0
0.01
0.02
0.03
0.04
0.05


x Diesel idle
o Diesel load
10^9
10^7
10^5
10^3
10^1
10^{-1}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
10^0
Scattering vector q [Å^{-1}]

Unified USAXS fit



Do soot primary particles have porosity ?



Referee raised question whether soot has porosity or not, i.e. the primary particles. Comparison of USAXS data from soot and glassy carbon, which has a high micro porosity.